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Synthesis and Magnetic Characterization of Metal-filled Double-sided Porous Silicon Samples

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Abstract A magnetic semiconductor/metal nanocomposite with a nanostructured silicon wafer as base material and incorporated metallic nanostructures (Ni, Co, NiCo) is fabricated in two electrochemical steps. First, the silicon template is anodized in an HF-electrolyte to obtain a porous structure with oriented pores grown perpendicular to the surface. This etching procedure is carried out either in forming a sample with a single porous layer on one side or in producing a double-sided specimen with a porous layer on each side. Second, this matrix is used for deposition of transition metals as Ni, Co or an alloy of these. The achieved hybrid material with incorporated Ni- and Co-nanostructures within one sample is investigated magnetically. The obtained results are compared with the ones gained from samples containing a single metal.

Keywords Nanocomposite material · Ferromagnetic nanostructures · Paramagnetic behaviour

Introduction

Ferromagnetic nanostructures are an important part in basic research but also in nanotechnological applications like magneto-optical devices, high density data storage, and also in biomedicine such structures at the nanoscale are promising candidates for example in drug delivery, imaging or targeting of special cells. Large area fabrication of periodically arranged nanostructures by self-organization has been carried out in using anodized porous alumina as template for depositing ferromagnetic nanowire arrays [1]. Magnetic characteristics of such metal-filled membranes have been investigated extensively [2]. The use of porous templates for embedding ferromagnetic materials increases the coercivity and squareness of hysteresis loops compared to thin metal films. Magnetic materials in the nanometre scale exhibit changed properties compared to bulk material and therefore offer great potential for nanotechnological applications. The nanoscopic systems consist of either particles or wires with magnetic properties due to their geometry and arrangement. In general, for applicability of the system, the magnetic nanostructures need to be ferromagnetic at room temperature. In some cases, a high anisotropy between the two magnetization directions, perpendicular and parallel to the surface, is of interest, and thus needle-like structures are favourable due to their high demagnetizing field. Furthermore, the interaction among the nanowires, which is mainly caused by dipolar coupling, is investigated [3]. One method to achieve low-dimensional structures is the deposition of metal nanostructures on patterned surfaces or into porous membranes with channels perpendicular to the surface, and therefore the arrangement of the metal structures exhibit a high spatial density with respect to the sample surface. Templates like porous alumina or polycarbonate foils are usually electrochemically fabricated and afterwards filled with a magnetic material by electrochemical deposition. In commercial microelectronics, most devices are based on silicon technology and thus for compatibility a silicon substrate is a precondition for applicability. Therefore, the employment of silicon as base material is of interest. Semiconducting/ferromagnetic composite systems that operate at room temperature are

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required. The presented nanocomposite, consisting of a porosified silicon matrix and embedded ferromagnetic nanostructures can be tuned in their magnetic behaviour by controlling the electrochemical deposition parameters.

Experiments

As template for the incorporation of ferromagnetic nanostructures, porous silicon (PS) offering morphologies in the meso/macro porous regime is used. For the preparation of single-sided as well as for double-sided porous silicon, a double-tank electrolytic cell is utilized with HF-solution on both sides. The electrolyte also acts to contact the anodic side of the sample. In the first case, a constant current density between 50 and 100 mA/cm^2 is employed, whereas the double-sided specimens are fabricated with an alternating current. The frequency is typically 0.1 Hz. Under these conditions, pore-diameters of 40 nm up to 80 nm can be achieved dependent on the applied current density [4]. For the presented investigations, PS-matrices with an average pore-diameter of 80 nm and an interpore-spacing of about 40 nm are used. The incorporation of the nanostructures is performed by electrochemical deposition of a metal from a metal salt solution. The metal deposition is carried out by pulsed deposition technique with frequencies between 0.025 and 0.1 Hz. The applied current density has been varied between 10 and 25 mA/cm^2. The electrolyte is composed of NiCl and $NiSO_4$ for Ni-deposition and of $CoSO_4$ for Co-deposition. To obtain a NiCo alloy, the Ni- and Co-salt solutions are mixed in the ratio 2:1 [5].

To achieve an extension of the nanosystem leading to novel magnetic behaviour, silicon wafers have been etched on both sides resulting in two porous layers of about 30 µm each. These double sided matrices, offering the same morphology on both sides are filled with either the same metal on both sides or with two different metals. To reduce the thickness of the remaining silicon bulk material in between the porous layers, the wafer has first been thinned down to about 45 µm and then been anodized on both sides (Fig. 1). Both layers offer a thickness of about 10 µm each, thus the remaining bulk silicon is 25 µm. The aim is to achieve samples with very thin layers of remaining bulk silicon (around ten nanometres) to investigate the magnetic interaction between the two layers.

The morphology and structure of the nanocomposite material is characterized by scanning electron microscopy. Magnetization measurements are performed by SQUID-magnetometry, whereas the sample with an area of 12 mm^2 is placed as usual within a straw, which is mounted on the sample holder. The magnetic field is applied either perpendicular or parallel to the sample surface that means in case of the investigated samples in easy axis or hard axis direction (parallel or perpendicular to the pores).

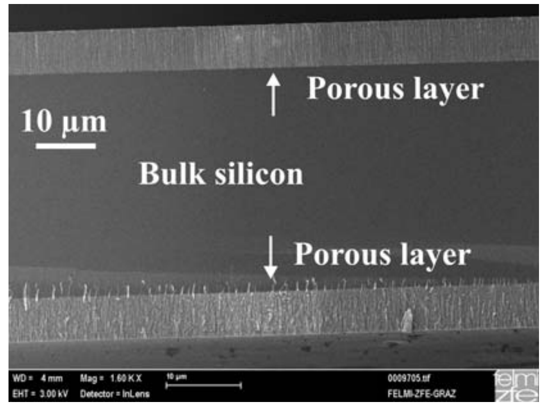

Fig. 1 Thinned silicon wafer with an entire thickness of about 45 µm porosified on both sides. The two porous silicon layers have a thickness of about 10 µm each

Results

Considering magnetization measurements of a porous silicon/metal nanocomposite, one sees that the magnetic behaviour is composed of two terms. A first one is observed at magnetic fields below the saturation magnetization of the incorporated metal. This behaviour is due to the ferromagnetic behaviour of the metal structures and strongly depends on the geometry of the precipitations. Samples containing mainly metal particles offer a higher coercivity but the magnetic anisotropy is less than for specimens containing more needle-like structures [4]. Comparing Ni and Co-filled samples, one can see that in both cases, the dependence on the geometry is similar. In case of particles deposited within the pores, having a similar spatial distribution for both materials, different magnetic anisotropy is observed. In case of deposited Ni-particles, the anisotropy between the two magnetization directions is about 50%, whereas in case of Co particles of similar size and density of the spatial distribution, the anisotropy is in the range of only 10%. This indicates that the Ni particles strongly interact along the pores in contrast to the Co particles, which seem more or less uncoupled [5].

Figure 2 shows a scanning electron micrograph, gained from back scattered electrons, of a double-sided porous silicon sample. One side is filled with Ni, the other one with Co. The hysteresis loop of this sample exhibits two different slopes caused by the different saturation magnetization of the two deposited metals. First, up to a field of 500 Oe, the ferromagnetic behaviour of Ni is dominant, and above the saturation of the Ni-structures, the behaviour of the Co structures, which are saturated at higher fields, becomes more distinctive (Fig. 3).

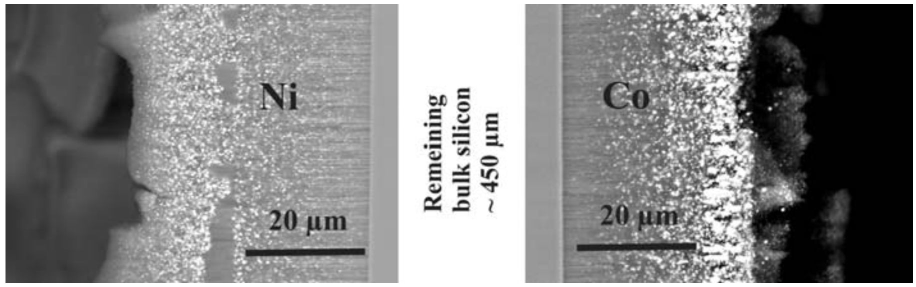

Fig. 2 SEM-image gained from the back scattered electrons shows the cross section of the two porous layers of a double-sided sample. One side is filled with Ni, the other one with Co. The remaining bulk silicon layer between the two layers is about 450 µm, which is not shown in the picture

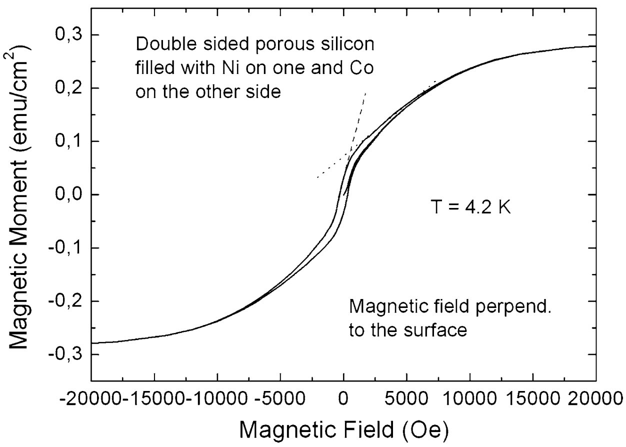

Fig. 3 Magnetization measurements performed on a double sided etched porous silicon sample, whereas the two porous layers are filled with two different metals, namely Ni and Co. Due to the distinct saturation magnetization of the two deposited metals, the hysteresis loop shows two different slopes

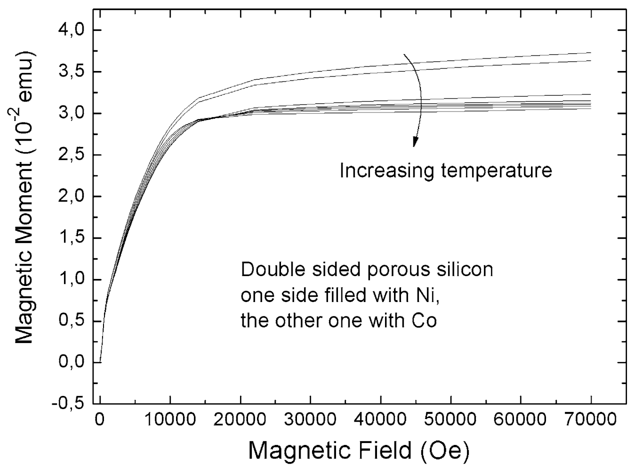

Fig. 4 Non-saturating term occurring at high magnetic fields above the saturation magnetization of the deposited metal measured on a double-sided sample with two different metals deposited (Ni, Co). The measurements are performed between 4.2 and 310 K with an applied magnetic field perpendicular to the sample surface. A temperature dependence is observed showing a decrease in the magnetization with increasing temperature

A further magnetic term is observed at magnetic fields greater than the saturation magnetization of the incorporated metal. In this high field region up to an available field of 7 T, the samples show an enhancement of the magnetization with increasing magnetic field without saturation. This non-saturating magnetization term is observed independent of the shape of the embedded metal-structures [6]. Above the saturation magnetization of the incorporated metal, the magnetization measured at a certain field decreases with increasing temperature. The temperature dependence of the high field term shows a paramagnetic-like behaviour and follows exactly the Curie–Weiss law. The non-saturating increase in the magnetization with the applied magnetic field is independent on the geometry of the deposited metal structures but strongly depends on the kind of deposited metal and is much less for Co than for Ni [6].

Considering samples with a porous silicon layer on each side and both of them filled with a different metal (Ni, Co), one can also observe this non-saturating term at high magnetic fields, which is a mixture of the contributions of both materials. In Fig. 4, this term occurring additionally to the ferromagnetic behaviour is shown. For all investigated samples, Ni-, Co- and Ni/Co-filled, this unexpected non-saturating high-field term exhibits an enhancement with increasing magnetic field, which is nearly linear, measured at temperatures above 80 K. The occurrence of this additional high-field contribution is still not completely understood but there are hints to be caused by orbital currents in the silicon skeleton [7].

A new kind of magnetism is also observed by some groups in usually diamagnetic systems as thiol capped gold-nanoparticles or thin gold layers [8] caused by a strong spin–orbit coupling due to a broken symmetry at the surface. An enhancement of the orbital moment and the magnetic anisotropy by a tetragonal distortion of the lattice of FeCo-alloy films is demonstrated by [9]. Recently, a unique kind of giant magnetic behaviour observed in organic monolayers is explained by Bose condensation of the electrons into a single low angular momentum quantum state caused by triplet pairing [10]. The occurring paramagnetism is explained by an internal angular momentum. Considering the PS/metal composite, the occurrence of the non-saturating paramagnetic term could be explained by an interface magnetism caused by triplet-pairing of carriers injected into the Si-skeleton. The resulting orbital moment leads to the paramagnetic behaviour of the specimens.

Conclusion

The presented nanocomposite is fabricated during a low-cost two-step electrochemical process. Porous silicon, tunable in its morphology, acts as template for the incorporation of ferromagnetic nanostructures. The silicon wafers are either anodized on a singe side or on both sides and subsequently filled with Ni, Co or both materials, one on each side. A sophisticated extension of this preparation technique is the etching and filling of double-sided porous silicon specimens in using ultrathin silicon wafers with an entire thickness of about 45 μm. The scope of preparing such samples is the investigation of the mutual magnetic influence of the two metal-filled porous layers. For this purpose, the remaining bulk silicon in between the two porous layers has to be in the range of 10 nm that could not have reached so far.

Furthermore, the investigated semiconductor/metal nanocomposites exhibit two characteristic magnetic terms, a first one at magnetic fields below the saturation magnetization of the incorporated metal, which is due to the ferromagnetism of the metal structures and a second one at higher fields, above the saturation magnetization. This additional occurring magnetic high field term is paramagnetic-like and shows a temperature dependence following the Curie–Weiss law. This unexpected property is observed for single-sided samples as well as for double-sided specimens filled with one metal or with two different metals. In case of double-sided samples, the magnetic behaviour is a mixture of both, caused by the deposited Ni-structures and the Co precipitates.

Because the metal deposition can be strongly influenced by the process parameters, samples with desired ferromagnetic properties as magnetic anisotropy, remanence and coercivity can be fabricated. In this low field region, the magnetic behaviour is strongly correlated with the structural and morphological features of the specimens and depends on the size, shape and spatial distribution of the deposited metal structures. In contrast, the unexpected term at high magnetic fields is independent of the geometry of the metal precipitations. The enhancement of the magnetization with the applied field is less in case of Co compared to Ni and is more or less linear above 80 K.

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References

1. H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, Appl. Phys. Lett. **71**, 2770 (1997)
2. M. Vazquez, K. Pirota, J. Torrejon, D. Navas, M. Hernandez-Velez, J. Mag. Mag. Mat. **294**, 174 (2005)
3. M. Vazquez, K. Pirota, M. Hernandez-Velez, V.M. Prida, D. Navas, R. Sanz, F. Batallan, J. Velazquez, J. Appl. Phys. **95**, 6642–6644 (2004)
4. P. Granitzer, K. Rumpf, P. Pölt, S. Simic, H. Krenn, Phys. Stat. Sol. (c) **5**, 3580 (2008)
5. K. Rumpf, P. Granitzer, P. Pölt, S. Simic, H. Krenn, Phys. Stat. Sol. (c) **5**, 3798 (2008)
6. K. Rumpf, P. Granitzer, P. Pölt, H. Krenn, Phys. Stat. Sol. (c) (2009) (in press)
7. S.D. Ganichev, E.L. Ivchenko, V.V. Belkov, S.A. Tarasenko, M. Solinger, D. Weiss, W. Wegscheider, W. Prettl, Nature **417**, 153 (2002)
8. A. Hernando, P. Crespo, M.A. Garcia, Phys. Rev. Lett. **96**, 057206 (2006)
9. F. Yildiz, F. Luo, C. Tieg, R.M. Abrudan, X.L. Fu, A. Winkelmann, M. Przybylski, J. Kirschner, Phys. Rev. Lett. **100**, 037205 (2007)
10. Z. Vager, R. Naaman, Phys. Rev. Lett. **92**, 087205 (2004)